

WE CLAIM:

1. An ultra-thin integral composite membrane comprising:
(a) a porous membrane having a microstructure of micropores of polymer with a porosity of greater than 35%, an average pore diameter of less than 10 μm and a thickness of at most 0.025 mm; and
(b) a perfluoro ion exchange material impregnated within the micropores of the polymeric membrane so as to render them substantially occlusive, wherein the composite membrane is substantially free of pinholes.
2. An ultra-thin integral composite membrane as described in Claim 1 wherein the porous polymeric membrane is selected from the group including perfluoroalkyloxy resin, fluorinated ethylene propylene, polyolefins, polyamides, cellulosics, polycarbonates, fluorinated and chlorinated polymers, and polysulfones.
3. An ultra-thin integral composite membrane as described in Claim 1 wherein the porous polymeric membrane is expanded porous polytetrafluoroethylene.
4. An ultra-thin integral composite membrane as described in Claim 1 wherein the perfluoro ion exchange material is selected from the group including perfluorinated sulfonic acid resin, perfluorinated carboxylic acid resin, polyvinyl alcohol, divinyl benzene, and styrene-based polymers.
5. An ultra-thin integral composite membrane as described in Claim 1 wherein the perfluoro ion exchange material is a perfluorosulfonic acid/tetrafluoroethylene copolymer resin dissolved in a solvent solution selected from the group including water, ethanol, propanol, butanol, methanol, and combinations thereof.
6. An ultra-thin composite membrane as described in Claim 1 further comprising a reinforcement backing bonded to the porous polymeric membrane, wherein the reinforcement backing is selected from the group including woven and nonwoven materials
7. An ultra-thin composite membrane as described in Claim 6 wherein the woven materials are selected from the group including: weaves of expanded porous polytetrafluoroethylene fibers, webs of polypropylene, and netting of polypropylene.
8. An ultra-thin composite membrane as described in Claim 6 wherein the nonwoven material is spun-bonded polypropylene.
9. An ultra-thin composite membrane comprising:

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- (a) a porous membrane having a microstructure of micropores of polymer with a porosity of greater than 35%, an average pore diameter of less than 10 µm and a thickness of at most 0.025 mm; and
- 5 (b) a perfluoro ion exchange material fully impregnated within the micropores of the polymeric membrane so as to render them fully occlusive, wherein the composite membrane is air impermeable with a Guiney number of infinity, and is substantially free of pinholes.
- 10 10. An ultra-thin composite membrane as described in claim 9 wherein the porous polymeric membrane is selected from the group including perfluoroalkyloxy resin, fluorinated ethylene propylene, polyolefins, polyamides, cellulosics, polycarbonates, fluorinated and chlorinated polymers, and polysulfones.
- 15 11. An ultra-thin integral composite membrane as described in Claim 9 wherein the porous polymeric membrane is expanded porous polytetrafluoroethylene.
12. An ultra-thin integral composite membrane as described in Claim 9 wherein the perfluoro ion exchange material is selected from the group including perfluorinated sulfonic acid resin, perfluorinated carboxylic acid resin, polyvinyl alcohol, divinyl benzene, and styrene-based polymers.
- 20 13. An ultra-thin integral composite membrane as described in Claim 9 wherein the perfluoro ion exchange material is a perfluorosulfonic acid/tetrafluoroethylene copolymer resin dissolved in a solvent solution selected from the group including water, ethanol, propanol, butanol, methanol and combinations thereof.
- 25 14. An ultra-thin composite membrane as described in Claim 9 further comprising a reinforcement backing bonded to the porous polymeric membrane, wherein the reinforcement backing is selected from the group including woven and nonwoven materials
- 30 15. An ultra-thin composite membrane as described in Claim 14 wherein the woven materials are selected from the group including: weaves of expanded porous polytetrafluoroethylene fibers, webs of polypropylene, and netting of polypropylene.
- 35 16. An ultra-thin composite membrane as described in Claim 14 wherein the nonwoven material is spun-bonded polypropylene.
17. A method of making an ultra-thin composite membrane comprising the steps of:

- 5 (a) mixing a solution of a perfluoro ion exchange material and a surfactant having a molecular weight greater than 100; and
 (b) impregnating the solution into a porous polymeric membrane having a microstructure of micropores of polymer having a thickness of less than 0.025 mm so as to occlude at least 90% of the pores of the membrane;
- 10 18. A method of making an ultra-thin composite membrane as described in Claim 17 further comprising the steps of:
- 15 (c) soaking the impregnated membrane in a low molecular weight alcohol to remove the surfactant;
 (d) drying the membrane in an oven to an elevated temperature; and
 (e) boiling said membrane in a swelling agent causing the membrane to swell.
- 20 19. A method of making an ultra-thin composite membrane as described in Claim 17 wherein the solution is impregnated through the entire thickness of the porous polymeric membrane so as to occlude all of the pores.
- 25 20. A method of making an ultra-thin composite membrane as described in Claim 17 further comprising an initial step of laminating a reinforcement material to the porous polymeric membrane before the mixing and impregnating steps.
- 30 21. A method of making an ultra-thin composite membrane as described in Claim 17 further comprising a step of selecting a porous polymeric membrane from the group including perfluoro alkyloxy resin, fluorinated ethylene propylene, silicone, cellulose, and expanded porous polytetrafluoroethylene.
- 35 22. A method of making an ultra-thin composite membrane as described in Claim 17 further comprising the step of selecting a perfluoro ion exchange material from the group including perfluorinated sulfonic acid resin, perfluorinated carboxylic acid resin, polyvinyl alcohol, divinyl benzenes, and styrene-based polymers.
23. A method of making an ultra-thin composite membrane as described in Claim 17 further comprising the step of selecting a surfactant having a molecular weight of greater than 100 from the group including: anionic, nonionic, and amphoteric surfactants.

24. A method of making an ultra-thin composite membrane as described in Claim 18 further comprising the step of selecting a lower molecular weight alcohol for removing the surfactant from the group including isopropanol, methanol, and glycerin.
- 5 25. A method of making an ultra-thin composite membrane as described in Claim 17 wherein the impregnating step is selected from the group including forward roll coating, reverse roll coating, gravure coating, doctor coating, kiss coating, dipping, brushing, painting and spraying.
- 10 26. A process for regenerating an ultra-thin composite membrane of a porous polymeric membrane that has been impregnated with a perfluoro ion exchange material comprising the steps of:
- (a) selecting a strong acid from the group including nitric and chromic acids; and
- (b) boiling said composite membrane with the strong acid.
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